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ARTICLES

Selective Voltammetric and Flow-Injection Determination of Guanosine and Adenosine at a Glassy Carbon Electrode Modified with a Ruthenium Hexachlororuthenate Film

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Abstract—An inorganic film of ruthenium hexachlororuthenate ($RuRuCl_6$), deposited on the surface of a glassy carbon electrode, exhibits electrocatalytic activity in the oxidation of purine nucleosides, such as guanosine and adenosine. Appropriate operating conditions are found for fabricating a polymer film on the surface of glassy carbon and for recording the maximum electrocatalytic current for the modified electrode. A method for the selective voltammetric determination of guanosine and adenosine in their simultaneous presence at an electrode modified by a $RuRuCl_6$ film is developed. A procedure is proposed for the amperometric detection of purine nucleosides with this modified electrode under the conditions of flow-injection analysis. The linear dependence of the analytical signal on the concentration of guanosine and adenosine is observed up to 5×10^{-6} M in the stationary mode and up to 5×10^{-7} M in the flow system. The proposed method for the selective determination of guanosine and adenosine was tested in the analysis of human urine.

Keywords: chemically modified electrodes, inorganic polymer films, ruthenium hexachlororuthenate, guanosine, adenosine, electrocatalysis, electroanalysis, flow-injection analysis

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Purine bases associated with deoxyribose through an α-glycosidic bond belong to the class of purine nucleosides known for their metabolic and biological properties. Purine nucleosides, guanosine and adenosine, which are a part of nucleic acids, are of great biological importance. For example, adenosine models the physiological functions in the heart and urine, regulates the delivery of oxygen in cells under stress [1], and participates in the regulation of renal function [2]. Guanosine plays a protective role in cerebral ischemia [3] and promotes RNA splicing [4]. Deviations of their concentration from normal indices in biological fluids can indicate the development of viral diseases [5, 6]. The high concentration of adenosine and guanosine in urine is one of the diagnostic criteria for oncological diseases [7, 8]; a change in the level of these compounds in blood plasma is a diagnostic marker in studies of viral liver diseases [9]. All this points to the urgency of creating new ways to determine guanosine and adenosine for medical diagnosis.

Various methods for the simultaneous detection of adenosine and guanosine in biological fluids are known. The chromatographic determination of these nucleosides in the simultaneous presence was described [10–12]. It should be noted that although chromatographic methods are selective and sensitive, they include a prolonged stage of sample preparation. Compared to chromatographic methods, electrochemical methods are distinguished by high sensitivity, rapidity, simplicity of the experiment, and low cost of apparatus and, as a consequence, the overall analysis [13–15]. The direct oxidation of guanosine and adenosine at unmodified electrodes proceeds irreversibly and under overvoltage, which is because of slow electron transfer in the oxidation of these purine bases. This leads to the low selectivity and sensitivity of their voltammetric determination [16, 17]. The use of chemically modified electrodes (CMEs) based on the principles of electrocatalysis eliminates these shortcomings [18, 19]. For the voltammetric determination of guanosine and adenosine, ionic liquids [20, 21], carbon nanotubes [22, 23], and allotropic forms of carbon such as graphene [24], fullerene [25], and boron-doped diamond [26] are used as modifiers for CMEs.

An analysis of publications shows that, at present, much attention is paid to the development of voltammetric methods for the determination of a wide range of organic compounds using CMEs based on inorganic conducting polymer films, functioning on the principles of electrocatalysis. Hexachlorometallates are used as such films [27–32]. This is because of the ease of formation of such films on the electrode surface and the electrochemical generation of several cat-